

# **LIQUID HYPERGOLIC PROPELLANT**

## **FIELD OF THE INVENTION**

The present invention provides a liquid hypergolic propellant. In particular, a liquid hypergolic propellant is provided, containing reactive metals and/or reactive metal salts, and one or more liquid fuels, which is hypergolic when combined with an oxidizer.

## **BACKGROUND OF THE INVENTION**

Liquid hypergolic propellants are fuels with ignite with no ignition source, when mixed with a specific oxidizer. Such fuels are conventionally used in rocket engines, wherein the propellant and the oxidizer are atomized and sprayed into the combustion chamber, where the two components react on a molecular level and ignite.

A sensitizer may be added to the fuel, which acts to lowers the ignition delay of the fuel. In addition, gelling agents are sometimes used to gel the liquid propellant.

Conventional liquid hypergolic fuels are composed of an oxidizer and fuel. Common oxidizers include nitrogen tetroxide (NTO), inhibited fuming red nitric acid (IRFNA), nitric acid, chlorine trifluoride, and concentrated hydrogen peroxide. Common corresponding fuels include monomethyl hydrazine, unsymmetrical dimethyl hydrazine, and hydrazine, respectively.

Traditional hypergolic propellants, such as IRFNA, NTO, and members of the hydrazine family are very energetic, but are toxic and/or carcinogenic. Due to these hazards, such propellants are not only dangerous to people, but are expensive and

hazardous to transport, handle and use. As such, there has been a desire to find non-toxic hypergolic fuels.

Non-toxic hypergolic fuels using highly concentrated solutions of hydrogen peroxide as an oxidizer have been created and tested. These fuels are catalytic, meaning that they contain dissolved or suspended hydrogen peroxide catalysts. Upon contact with these catalysts, the hydrogen peroxide decomposes into superheated steam and oxygen, which then ignites the fuel.

Unfortunately, these hydrogen peroxide catalysts can reduce the performance of the fuels. Since these catalysts are generally derived from transition metal salts, they are composed of large atomic weight atoms, such as copper and iron. Combustion products of these heavy atoms reduce the velocity of the rocket exhaust, and reduce specific impulse. However, to reduce ignition delay, or the time between fuel and oxidizer contact and ignition, larger amounts of catalyst may be needed. Therefore, these catalysts are both beneficial and damaging to the performance of the fuel.

#### SUMMARY OF THE INVENTION

In order to achieve the objects of the present invention mentioned above, in a first embodiment, a liquid hypergolic propellant is provided comprising:

- (a) reactive metals and/or reactive metal salts; and
- (b) one or more liquid fuels,

wherein the propellant comprising (a) and (b) is hypergolic when combined with an oxidizer.

In a second embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment above is provided, further comprising (c) a sensitizer.

In a third embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment above is provided, further comprising (d) a gelling agent.

In a fourth embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment above is provided, wherein the reactive metals and/or reactive metal salts are defined by Formula I as follows:



wherein A is one or more of any of Li, Na, and K; M is one or more of any of B, C, and Al; H is H; x is 0-3, y is 0 or greater, and z is 0 or greater, and wherein when x is 0, y is 1, and when y is 0, x is 1.

In a fifth embodiment of the present invention, a liquid hypergolic propellant according to the fourth embodiment above is provided, wherein the reactive metals and/or the reactive metals salts are selected from the group consisting of simple hydrides, complex hydrides or organolithium compounds.

In a sixth embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment above is provided, wherein the fuels comprise one or more of hydrocarbons, alcohols, ketones, ethers, and/or aldehydes.

In a seventh embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment above is provided, wherein the fuels are defined by the following Formula II as follows:



wherein x is 0-8, y is 1-18, z is 0-4, and v is 0-5, and wherein when x is 0, v is 1 or greater.

In an eighth embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment is provided, wherein the sensitizer comprises one or more of amines, azides, and/or amides.

In a ninth embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment above is provided, wherein the sensitizer is defined by Formula III as follows:



wherein x is 1-8, y is 1-18, and z is 0-4.

In a tenth embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment above is provided, wherein the gelling agent comprises silica gel, guar, agar or starch.

In an eleventh embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment above is provided, wherein the reactive metals and reactive metal salts together comprise from 0.1-50.0 weight percent of the propellant.

In a twelfth embodiment of the present invention, a liquid hypergolic propellant according to the first embodiment above is provided, wherein the fuel comprises 50.0-99.9 weight percent of the propellant.

In a thirteenth embodiment of the present invention, a liquid hypergolic propellant according to the second embodiment above is provided, wherein the sensitizer comprises 0.1-40.0 weight percent of the propellant.

In a fourteenth embodiment of the present invention, a liquid hypergolic propellant according to the third embodiment above is provided, wherein the gelling agent comprises 0.1 – 20.0 weight percent of the propellant.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graphical illustration of the vacuum specific impulse, or  $I_{sp}$ , over a range of O/F values for Fuel A and Fuel B of the present invention versus conventionally used NTO/MMH, the data obtained using the United States Air Force Specific Impulse Code.

## DETAILED DESCRIPTION OF THE INVENTION

Traditional hypergolic propellants are very energetic but are also toxic, carcinogenic or both. Recently developed non-toxic or low-toxicity hypergolic fuels using rocket grade hydrogen peroxide (80% or higher) are successful, but generally produce less specific impulse than NTO/MMH and ignite more slowly. These new hypergolic fuels rely on the use of dissolved transition metal catalytic salts to trigger the ignition. Substantial amounts of such salts may be required to achieve self-ignition, but such large amounts of these metal compounds can reduce specific impulse.

To address and overcome the deficiencies of the traditional, as well as more recent, hypergolic fuels, the present invention provides a liquid hypergolic propellant comprising reactive metals and/or reactive metal salts, and one or more liquid fuels. The resulting propellant is hypergolic when combined with an oxidizer. In addition, a sensitizer may be added to lower the ignition delay. Further, a gelling agent may be added thereto to allow the suspension of reactive metals or reactive metal salts in the propellant.

The reactive metals and/or reactive metal salts of the present invention are defined by Formula I as follows:



wherein A is one or more of any of Li, Na, and K; M is one or more of any of B, C, and Al; H is H; x is 0-3, y is 0 or greater, and z is 0 or greater, and wherein when x is 0, y is 1, and when y is 0, x is 1. For example, the reactive metals and/or the reactive metals

salts may be simple hydrides, complex hydrides or organolithium compounds. Preferably, the reactive metals and reactive metal salts together comprise from 0.1-50.0 weight percent of the propellant.

The fuels of the present invention are defined by the following Formula II as follows:



wherein x is 0-8, y is 1-18, z is 0-4, and v is 0-5, and wherein when x is 0, v is 1 or greater. For example, the fuels may comprise one or more of hydrocarbons, alcohols, ketones, ethers, and/or aldehydes. Preferably, the fuel comprises 50.0-99.9 weight percent of the propellant. the sensitizer comprises 0.1-40.0 weight percent of the propellant.

The sensitizer of the present invention is defined by Formula III as follows:



wherein x is 1-8, y is 1-18, and z is 0-4. For example, the sensitizer may comprise one or more of amines, azides, and/or amides.

The gelling agent described above may comprise silica gel, guar, agar or starch. Preferably, the gelling agent comprises 0.1 – 20.0 weight percent of the propellant.

The fuels of the present invention overcome the deficiencies of both the traditional hypergols and the newer catalytic hypergols by the use of reactive metal

species described above. These compounds combust directly and non-catalytically with hydrogen peroxide, and because they are composed of light metals, they do not reduce the thermodynamic performance of the fuel as the catalytic salts do. Therefore, adding more reactive metal species to the fuel of the present invention can increase the specific impulse and reduce ignition delay.

Each reactive hypergolic fuel of the present invention is created by directly mixing the energetic liquid, promoter (if necessary), and the reactive metal species under an inert atmosphere such as argon. Preparation of the fuels must be performed in an inert atmosphere, as the reactive metal compounds are often air and moisture sensitive.

To verify the advantages of the reactive metal fuels of the present invention over the conventional hypergolic fuels, the hypergolic ignition characteristics of two fuels (Fuel A and Fuel B) according to the present invention were tested to determine their hypergolic ignition characteristics. The components of Fuel A and Fuel B are as follows:

Fuel A: 4.2% by weight of lithium borohydride (LBH) in tetrahydrofuran (THF)

Fuel B: 20% by weight solution of lithium aluminum hydride (LAH) in diethyl ether

Both Fuel A and Fuel B were experimentally hypergolically tested with 97% hydrogen peroxide using a conventional drop test device to measure the ignition characteristics thereof. Both fuels ignited rapidly.

Both Fuel A and Fuel B were compared to nitrogen tetroxide (NTO) / monomethyl hydrazine (MMH) thermodynamically, by using the United States Air Force Specific Impulse Code, which is a computer code which theoretically models the thermodynamic performance of a rocket propellant combination. Figure 1 illustrates the

vacuum specific impulse, or  $I_{sp}$ , over a range of O/F values for Fuel A and Fuel B versus the NTO/MMH, the data being obtained using the United States Air Force Specific Impulse Code. For this comparison, a chamber pressure of 500 psi and an expansion ratio of 10 were used.

As illustrated in Figure 1, the theoretical  $I_{sp}$  of both reactive fuel combinations of the present invention approach the performance of NTO/MMH, with both reaching peak performance at an O/F about 5. Also, due to the high O/F optimum values and the density of RGHP, the density specific impulse values of these fuels may exceed that of NTO/MMH. Although these fuels did not theoretically outperform NTO/MMH, fuels described by this invention which are comprised of more energetic liquids and higher concentrations of such reactive compounds than Fuels A and B have the potential to exceed the thermodynamic performance of NTO/MMH while being less toxic. The fuels described by this invention could replace NTO/MMH in divert and attitude control applications, especially where minimal toxicity is required.

#### IGNITION DELAY TESTING

Ignition delay testing for a fuel of the present invention, as well as the conventional Navy Block 0 fuel, was performed using a high-speed video camera and using the a device called a Hypertester, which can determine the ignition delay value of a propellant combination to within one millisecond. The fuel of the present invention, referred to herein as Fuel A, defined above as comprising 4.2% by weight lithium borohydride and 95.8% by weight tetrahydrofuran, and U.S. Navy Block 0, which has the following composition:

Navy Block 0: 78% methanol and 22% manganese (II) acetate tetrahydrate

The Hypertester, developed at Purdue University, is simply a drop-test device which uses an oscilloscope to record the timing of events characterizing ignition delay. To determine the ignition delay, a specified amount of fuel is placed in the crucible (approximately 20 microliters). A drop of oxidizer (20 to 30 microliters) falls from its syringe suspended above the crucible. When the drop impacts the crucible, the velocity transducer senses the impact and transmits the vibration to the oscilloscope. When the fuel and oxidizer ignite, the light given off is detected by the photodiode, and this data is also transmitted to the oscilloscope on a separate channel. The time between the impact of the oxidizer drop and the beginning of the flash from the combustion is recorded as the ignition delay.

Using 96.8% hydrogen peroxide, Fuel A was tested in the Hypertester, as was U.S. Navy Block 0, an early catalytic hypergolic fuel developed at China Lake. Block 0 was tested for comparison. Five hypergolic ignition tests of each of Fuel A and Block 0 were conducted. The average ignition delay for Block 0 was 11.2 milliseconds with the values ranging between 9 and 13 milliseconds. In contrast, for Fuel A, the fuel of the present invention, the average ignition delay was 3 milliseconds with no measurable deviation. Such a small delay for this fuel is competitive with NTO/MMH, which has produced an ignition delay of less than 3 milliseconds using the same device (the Hypertester). In an engine, the difference in ignition delay between RGHP/LBH fuel (Fuel A) (RGHP is rocket grade hydrogen peroxide, which is defined as a solution of

hydrogen peroxide and water consisting of at least 90% hydrogen peroxide with a minimum concentration of stannic and phosphate stabilizers) and NTO/MMH should be even less as the propellants collide together under high pressure.

Using a high-speed video camera, the ignition process of RGHP/Block 0 and Fuel A was visible. The high-speed video camera captured video of a drop test of each combination at a rate of 1000 frames per second. For Block 0, a catalytic hypergolic fuel, the high-speed camera displayed the influence of the fluid properties upon the ignition delay. After the drop of peroxide impacted the fuel in the crucible, a vapor cloud of fuel, oxygen, and water vapor began to expand from the impact point. The ignition of this cloud occurred more than an inch above the impingement point. Once the initial combustion occurred, the flame spread rapidly throughout the cloud. In contrast, the ignition of Fuel A was much more rapid. In particular, no fuel and oxidizer cloud was noted before the ignition.

The ignition tests described above indicate that the ignition delay of Block 0 is limited by smaller amount of heat produced by the decomposition reaction as opposed to a combustion reaction, and the longer time required to heat the fuel and oxidizer vapor mixture to its ignition point after the decomposition takes place. Block 0 contains approximately 5% by weight of manganese, the active catalytic species, while the other fuel contains 4.2% by weight LBH. Therefore, the amounts of the active species in each fuel are comparable. And, even though the solvents are different, it is reasonable to say that Fuel A ignites much more rapidly due to the larger amount of heat produced by the combustion reaction of RGHP/LBH as opposed to the decomposition reaction of the RGHP. Because of the higher heat evolved, the ignition point of the remainder of the

LBH fuel is reached much faster. The decomposition reaction does not produce enough heat to ignite the remainder of the Block 0 as rapidly.

In order to reduce the ignition delay of Block 0, more of the catalytic salt would be needed. However, this would reduce the specific impulse. With the LBH fuel (Fuel A) and other such reactive hypergolic fuels, increasing the amount of the metal hydride has the potential to reduce the ignition delay and increase the Isp. This is the major advantage of reactive hypergolic fuels over catalytic hypergolic fuels.

### ENGINE TESTING

Open injector engine testing of both Fuel A and Fuel B of the present invention was performed at the Advanced Propellants and Combustion Lab at Purdue University using its 1000-lbf bipropellant test stand.

A 0.5 liter fuel tank and new plumbing were used to conduct these tests. All hardware was cleaned thoroughly with ethanol and then flushed with THF to remove the ethanol and to remove any other soluble material from the tank. The engine chosen was a pintle injector design. The open injector tests were performed to determine if the ignition delays produced by the fuels were suitable and to determine the appropriate fuel lead times to be used when the chamber and nozzle would be attached. All tests were recorded with a 1000 frame per second high speed camera. An effort was made to fire the fuels as quickly as possible after loading due to the highly reactive nature of the fuels. It was feared that any residual contaminants in the tank could react with the hydrides and reduce the ignition delay to unacceptable levels. The fuels were tested with 97.6%

hydrogen peroxide, and both fuels ignited rapidly, as could be seen with the high speed video camera. The results of the tests are summarized in Table I below.

**TABLE I**

Fuel	Test duration (s)	Average oxidizer inlet pressure (psi)	Average fuel inlet pressure (psi)	Total mass flow (lbm/s)	O/F	Ignition
<b>Fuel A</b>						
Test 1	3	260	240	0.645	4.92	rapid
Test 2	3	260	240	0.643	4.87	rapid
<b>Fuel B</b>						
Test 1	3	350	235	0.650	4.10	rapid
Test 2	3	350	250	0.649	4.09	rapid

The ignition characteristics displayed by both Fuel A and B in these tests indicate that they can be successfully fired in a full engine with the chamber and nozzle attached.

**Definitions:**

*Ignition Delay*: the time between fuel and oxidizer impingement and flame generation.

*Hypergolic fuel*: a fuel which ignites with no ignition source, when mixed with a specific oxidizer.

*Reactive Fuel*: a hypergolic fuel which is ignited by the oxidizer through a non-catalytic reaction.

*Sensitizer*: an additive which lowers the ignition delay of the fuel.

*Gelling Agent*: an additive used to gel the liquid propellant. It could actually be the reactive metal or reactive salt itself, or it could allow the suspension of reactive metals or reactive metal salts in the propellant.